1. Title: Kinetic study of oxidative degradation of organophosphorous pesticides in presence and absence of homogenous catalysts

2. Introduction

Toxicology is the study of the occurrence, properties, effects, detection and regulation of toxic substances and their effect on biological systems. It is multi-disciplinary subject, which covers many sub-disciplines including environmental toxicology.

Environmental toxicology is concerned primarily with the movement and impact of toxicants and their metabolites in the environment, in food chains, and upon the structure and function of biological systems. Various classes of toxic stressors found in the environment include metals, pesticides, aromatic and aliphatic hydrocarbons volatile organic compounds, particulates, radiation, and biological agents such as myco toxins and bacterial toxins [1].

Any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies is called pesticide [2].

The environmental contamination by organic pesticides has been a serious issue due to their popularity in use. They have been extensively applied to the agricultural activities as well as environmental sanitation implementation due to their chemical characteristics of toxicity, bioaccumulation and persistence [3, 4]. The residual pesticides may become the contamination sources and pose a serious threat to the soil and groundwater environment through the rainfall infiltration process. This contamination becomes even more serious when persistent organic compounds are involved. Among the often-used pesticides, organophosphorus are considered most detrimental to the environment because of their persistence and toxicity [5].

On the basis of chemical composition pesticides can be mainly classified as:

- Organophosphorous (Dimethoate, Phorate, Acephate)
- Organochlorines (BHC, DDT, PCP)
- Carbamates (Carbaryl, Propoxur)
- Dithiocarbamate (Zineb, Ziram)
- Organomercury (PMA, MEMC)
- Heterocyclic (Atrazine, Simazine)
- Phthalimide (Captan, Folpet)
- Nitro derivatives of phenols (DNOC, Dinobuton, Dinocap)
- Chlorophenoxy acids (2,4-D, 2, 4, 5-T)

"Organophosphates" refers to a group of insecticides or nerve agents acting on the enzyme acetyl cholinesterase (the pesticide group carbamates also act on this enzyme, but through a different mechanism). The term is used often to describe virtually any organic phosphorus containing compound, especially when dealing with neurotoxic compounds. Many of the so-called organophosphates contain C-P bonds. For instance, sarin is *O*-isopropyl methylphosphonofluoridate, which is formally derived from phosphorous acid, not phosphoric acid. Also, many derivatives of phosphinic acid which are neurotoxic.

Organophosphate pesticides irreversibly inactivate acetyl cholinesterase, which is essential to nerve function in insects, humans, and many other animals. Organophosphate pesticides affect this enzyme in varied ways, and thus in their potential for poisoning.

Commonly used organophosphorous pesticide include parathion, malathion, methyl parathion, chlorpyrifos, diazinon, dichlorvos, phosmet, fenitrothion,[6] tetrachlorvinphos, azamethiphos, and azinphos methyl. Malath ion is widely used in agriculture, residential landscaping, public recreation areas, and in public health pest control programs such as mosquito eradication [7].

To mitigate the soil and groundwater contamination by pesticides, many processes based on redox reactions initiated by hydroxyl radicals, have been reported as effective

alternatives compared to conventional treatment processes [5]. In these processes toxic waste is partially pretreated by oxidation technologies to produce intermediates that are more readily degradable. Many oxidation processes are currently employed for this purpose, including photochemical degradation processes, photo catalysis and chemical oxidation processes.

The aim of the present work is to study the kinetics of oxidative degradation of organophosphorous pesticide in presence and absence of homogenous catalysts.

3. BRIEF REVIEW OF THE WORK ALREADY DONE IN THE FIELD

Various analytical methods are reported for the identification of pesticides present in water, soil and environment. Navarro et al. [8] determined persistence of simazine and terbuthylazine and appearance of their principal dealkylated chloro-s-triazine metabolites in agricultural soil after adding urban sewage sludge as organic material. Fava et al. evaluated the mobility, persistence and leaching potential of some degradation products of alachlor and metolachlor. Lerch et al. [9] studied trifluralin metabolism pattern in a real contaminated soil. The formation and the transport of sulfonic acid metabolites of alachlor, metolachlor were established by Aga and Thurman [10]. Decomposition in soil and occurrence in ground water of the herbicide glyphosate was studied by Torstensson et al. [11]. Degradation of two model insecticides, diazinon and malathion was compared and studied in the environment by Bavcon et al. [12]. The photocatalyst titanium dioxide Degussa P-25 has been widely used in most of the experimental conditions, for degradation of toxic organic compounds by Bahnemann and sing et al. [13-16]. Puma et al. examined the effect of light wavelength on the photocatalytic degradation of 2-chlorophenol (2-CP) using UV radiation [17]. Parida and Parija examined the effect of initial substrate concentration (2-25g/l) on the photocatalytic degradation of phenol under sunlight, visible and UV light, respectively [18]. Lathasree et al. studied the effect of initial concentration (40-100ppm) on the photocatalytic degradation of phenol using ZnO as catalyst [19]. Organophosphorous pesticides determined by solid phase micro extraction (SPME) followed by gas chromatography with selected ion monitoring was reported by

Tomkins et al [20].

4. OBJECTIVE OF THE WORK

The main objective of the proposed research work is:

- To develop catalytic oxidative system for degradation of organophosphorous pesticide in presence of transition metals ions/metal nano particles.
- To synthesize and characterize new catalytic oxidative system.
- To study the factors that affect the reaction conditions such as concentration of substrate, concentration of catalyst, concentration of oxidant, temperature, pH of reaction medium, ionic strength, solvent effect, and investigate the kinetics.
- To study the thermodynamic activation parameters.
- To determine rate law, and to propose reaction mechanism which will be based on experimental observation.

5. NOTEWORTHY CONTRIBUTION IN THE FIELD OF PROPOSED WORK

Various simple and sensitive spectrophotometric methods have been reported in our laboratory for detection and determination of organophosphorous pesticides with molybdate and ethylene blue by flotation-dissolution method by Agrwal et al., Mathew et al. reported method for the determination of organophosphorous pesticides which is based on the oxidation of organophosphorous with N-bromosuccinimide and the unconsumed NBS is determined with rhodamine B [21], Tiwari et al. reported a method for the determination of organophosphorous pesticide in vegetable sample which is based on the catalytic effect of organophosphorous pesticide on oxidation of LCV by potassium iodate in acidic medium [22].

Arapoglou et al. reported the application of a direct electrochemical oxidation for the treatment of organophosphoric pesticides methyl parathion [23]. Vlyssides et al. reported the electrochemical degradation of methyl parathion by using Ti/Pt as anode in an aqueous medium of sodium chloride as electrolyte at 45ºC and an applied current

density of 560 mA/cm^2 [24]. Hachami et al. investigated the degradation of 1.4 mM of methidathion in aqueous solution by anodic oxidation using a boron-doped diamond (BDD) anode [25]. Yatmaz and Uzman investigated the direct electrochemical oxidation for removal of monochrotophos on Ti electrodes in aqueous solution of sodium salts (chloride or sulphate) as a function of applied current density and initial concentrations of pesticide [26]. Vlyssides et al. has also reported the electrochemical oxidation of the phosphorothioate pesticides Demeton-S-methyl, Methamidophos, Fenthion and Diazinon [27-28]. The anodic oxidation of methamidophos was studied by Martínez-Huitle et al. in a sodium sulphate aqueous solution on Pb/PbO_2, Ti/SnO_2, and Si/BDD (boron doped diamond) electrodes at 30°C [29].

The electrochemical oxidation of some thiocarbamate herbicides in aqueous NaCl solutions has been investigated F. Mogyoródy [30-31]. The oxidation of the atrazine herbicide has been investigated by Malpass et al. [32-33]. In addition, the electrochemical combustion of mecoprop by Flox et al. [34], carbaryl by Miwa et al., Malpass et al. [35-36], and propham herbicides by Ozcan et al. has also been reported recently [37].

In recent year, platinum group metal ions including Ru(III), Os(VIII), Ir(III), Rh(III), Pd(II), Pt(IV), and Au (III), are widely used as catalyst due to their strong catalytic influences in various reactions [38-40]. Generally, the mechanisms of catalysis depend on the nature of the substrate, oxidant (NBS, permanganate, persulphate, etc.), and other experimental conditions.

6. PROPOSED METHODOLOGY

The main aim of proposed work is kinetic study of oxidative degradation of organophosphorous pesticides in presence and absence of catalysts as homogenous medium.

The proposed methodology will be based on –

- To develop new oxidative reagent system involving transition metal/ ions as homogenous catalyst.
- Investigate the kinetics of the oxidative degradation of organophosphorous pesticide.
- Optimization of various parameters-

  Effect of pH- The effect of pH on the reaction rate will be studied during the progress of reaction because with the change in pH the extent of reaction may vary.

  Effect of temperature – The effect of temperature of reaction rate will be studied and optimized.

  Effect of time- The progress of reaction rate will be monitored at different time intervals and various kinetic parameters will be optimized.

  Effect of substrate-The amount of substrate must be study for setting all parameters.
- Characterization of various oxidation product/degradation products.
- Application of the oxidative reagent system for the degradation of various organophosphorous pesticides like parathion, malathion, methyl parathion, chlorpyrifos, diazinon etc.

7. EXPECTED OUTCOME OF THE PROPOSED WORK

Various innovative technologies have been proposed for the removal of organophosphorous pesticides namely photo catalytic oxidation, ultrasonic radiation, biodegradation and thermal adsorption by various research groups. These methods may be applied for degradation of various Organophosphorous pesticides. This in turn would help in characterization and monitoring of various pollutants generated by pesticides. The methods developed on the proposed methodology will be beneficial in combating with the present day pollution problem and can be easily used and adopted in routine labs for the degradation of pesticides. Such studies would also provide a new field of research and beneficial for society.

8. BIBLIOGRAPHY

1. Tetsuo satoh, Salmaan H. Inayat-Hussain, *"Environmental Toxicology and Human Health"- Vol.I,* Encyclopedia of Life Support Systems, 1998.
2. Food and Agriculture Organization of the United Nations, International Code of Conduct on the Distribution and Use of Pesticides (2002), Retrieved on 25-10-2007.
3. R. S. Adams, *Residue Reviews*, 1973, 47, 1-54.
4. W. D. Guenzi, J. L. Ahlrichs, M. E. Bloodworth, G. Chester, R. G. Nash, *Soil Science Society of America, Wisconsin*, 1974, 562.
5. E. Neyens, J. Baeyens, *Journal of Hazardous Materials*, 2003, 98, 33–55.
6. "Fenitrothion". *Pesticide Information Profiles*. Extension Toxicology Network. Sept 1995.
7. M.R. Bonner, J. Coble, A. Blair, *American Journal of Epidemiology*, 2007, 166 (9), 1023–34.
8. S. Navarro, N. Vela, C. Garcia, G. Navarro, *Journal of Agricultural and Food chemistry*, 2004, 51, 7359.
9. R.N. Lerch, I. Ferrer, E.M. Thurman, R.M. Zablotowicz, *American Chemical Society*, 2003, 291.
10. D.S. Aga, E.M. Thurman, *Environmental Science and Technology*, 2001, 35, 2455.
11. E. Bo6rjesson, L. Torstensson, *Journal of Chromatography A*, 2000, 886, 207.
12. M. Bavcon, P. Trebse, L. Zupancic-Kralj, *Chemosphere*, 2003, 50, 595.
13. W. Bahnemann, M. Muneer, Ma.M. Haque, *Catalysis Today*, 2007, 124, 133-148
14. R. Erquez, P. Pichat , *Journal of Environmental Science and Health Part A*, 2006, 41, 955–966.
15. H. K. Singh, M. Muneer, *Research on Chemical Intermediates*, 2004, 30(3), 317-329.
16. H.K.Singh, M.Saquib, M.Haque, M.Muneer, *Journal of Hazardous Materials*, 2007, 142, 374-380.
17. G.L. Puma, P.l. Yue, *Industrial and Engineering Chemistry Research*, 2002, 41, 5594-5600.
18. K.M. Parida, S. Parija, *Solar Energy*, 2006, 80, 1048-1054.
19. S. Lathasree, A.N. Rao, B. Siva Samlor, V. Sadasivam, K. Rengaraj, *Journal of Molecular Catalysis A: Chemical*, 2004, 223,101-105.
20. B.A. Tomkins, R.H. llgner, *Journal of Chromatography A*, 2002, 972, 183-194.

21. S.B Mathew, V.K Gupta, *Bulletin of the Chemical Society Ethiopia,* 2007, 21 (1), 1.
22. Tiwari et al., *Journal of the Brazilian Chemical Society*, 2012, 23 (2), 67-69.
23. D. Arapoglou, A. Vlyssides, C. Israilides, A. Zorpas, P. Karlis, *Journal of Hazardous Materials B*, 2003,98, 191-199.
24. A. Vlyssides, E.M. Barampouti, S. Mai, D. Arapoglou, A. Kotronarou, *Environmental Science and Technology*, 2004, 38, 6125-6131.
25. F. Hachami, R. Salghi, M. Mihit, L. Bazzi, K.Serrano, A. Hormatallah, M. Hilali, *International Scientific Journal for Alternative Energy and Ecology*, 2008, 6 (62), 35-40.
26. H.C. Yatmaz, Y. Uzman, *Journal of Electrochemical Sciences*, 2009, 4, 614-626.
27. A. Vlyssides, D. Arapoglou, S. Mai, E.M. Barampouti, *Chemosphere,* 2005, 58(4), 439-447.
28. A. Vlyssides, D. Arapoglou, S. Mai, E.M. Barampouti, *International Journal of Environmental and Pollution,* 2005, 23(3), 289-299.
29. C.A. Martínez-Huitle, A.De Battisti, S. Ferro, S. Reyna, M. Cerro, M.A. Quiroz, *Environmental Science and Technology*, 2008, 42, 6929-6935.
30. F. Mogyoródy, *Journal of Applied Electrochemistry*, 2006, 36(6), 635-642.
31. F. Mogyoródy, *Journal of Applied Electrochemistry*, 2006, 36(7), 773-781.
32. G.R.P. Malpass, D.W. Miwa, S.A.S. Machado, P. Olivi, A.J. *Journal of Hazardous materials,* 2006, 137(1) 565-572.
33. M. Mamián, W. Torres, F.E. Larmat, *Portugaliae Electrochimical Acta*, 2009, 27(3), 371-379.
34. C. Flox, P.L. Cabot, F. Centelas, J.A. Garrido, R.M. Rodríguez, C. Arias, E. Brillas, *Chemosphere* 64(6), 892-902.
35. D.W. Miwa, G.R.P. Malpass, S.A.S Machado, A.J. Motheo, *Water Research*, 2006, 40(17), 3281-3289.
36. G.R.P. Malpass, D.W. Miwa, A.C. Miwa, S.A.S. Machado, A.J. Motheo, *Journal of Hazardous Materials*, 2009, 167 (1-3), 224-229.
37. A. Ozcan, Y. Sahin, A.S. Koparal, M.A. Oturan, *Water Research*, 2008, 42(12), 2889-2898.
38. A.K. Singh, R. Negi, B. Jain, Y. Katre, S.P. Singh, *Industrial and Engineering Chemistry Research*, 2011, 50, 8407-8419.

39. A.K. Singh, R. Negi, B. Jain, Y. Katre, S.P. Singh, *Journal of molecular catalysis A; Chemical,* 2009, 302, 36-42.

40. A.K. Singh, R. Negi, B. Jain, Y. Katre, S.P. Singh, *Catalysis letter,* 2009, 312, 285-291.

39. A.K. Singh, R. Negi, B. Jain, Y. Katre, S.P. Singh, *Journal of molecular catalysis A; Chemical,* 2009, 302, 36-42.

40. A.K. Singh, R. Negi, B. Jain, Y. Katre, S.P. Singh, *Catalysis letter,* 2009, 312, 285-291.

Professor & Head
Department of Chemistry
V.Y.T.P.G. Autonomous
Durg (C.G.)

Signature of Supervisor

Pooja

Signature of Candidate

Forwarded

Chairman DRC

Principal
Govt. V.Y.T. P.G. Autonomous
College, Durg (C.G.)